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THE COLLEGE OF AERONAUTICS

CRANFIELD

Temperature Effects on Material Characteristics

- by -

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and

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SUMMARY

Some of the physical properties of the main elements of interest in high temperature technology are reviewed. Some general trends emerge when these properties are viewed as a function of melting point, but there are a few notable exceptions. Titanium, zirconium, niobium and tantalum all have disappointingly low moduli; chromium is excellent in many ways, but has a limited ductility at lower temperatures; molybdenum oxidises catastrophically above about 700°C, and niobium suffers from severe oxygen embrittlement. Beryllium and carbon (in the graphitic form) both stand out as exceptional materials, both have very low densities, beryllium a very high modulus but an unfortunately low ductility, while graphite has a relatively low strength at the lower temperatures, although at temperatures of 2000°C and above it emerges as a quite exceptional (and probably as the ultimate) high temperature material. Some of the fundamental factors involved in high temperature material development are examined, in the light, particularly, of past progress with the nickel alloys. If a similar progress can be achieved with other base elements then a considerable margin still remains to be exploited. Protection from oxidation at high temperatures is evidently a factor of major concern, not only with metals, but with graphite also. Successful coatings are therefore of high importance, and the questions they raise, such as bonding, differential thermal expansion, and so on, represent aspects of an even wider class covered by the term "composite structures". Such structures appear to offer the only serious solution to many high temperature requirements, and their design, construction and utilization has created a whole series of new exercises in materials assessment. Matters have become so complex, that a very radical and fundamental reassessment is required if we are to change, in any very significant way, the wasteful and ad hoc methods which characterise so much of present-day materials engineering.

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1. Introduction

In aeronautics and space technology, questions relating to the resistance of materials to temperature and stress may be classified in three main groups. Firstly, suitable skin materials are required to resist the very high kinetic heating which arises during re-entry into the earth's atmosphere. The missile problems are difficult enough, but the successful protection of a manned vehicle, which must necessarily be exposed to a much longer period of heating, raises materials questions of even greater difficulty. The same extreme conditions also apply to materials used in rocket motors. The second category embraces materials which can usefully raise the level of efficiency of propulsion units by making possible their successful operation at higher temperatures than at present. Gas turbine temperatures of 1000°C, for example, would constitute a significant advance. Finally, improved properties in the more conventional light alloys at temperatures above 100°C are of immediate concern to the aircraft industry as the structural materials in Mach 2 aircraft will certainly have to resist exposure to these temperatures over several thousands of hours - possibly thirty thousand or so. This last category is one which is not covered by the term "high temperature materials" in the usually accepted sense, and we shall not, therefore, give any attention to such alloys in the present paper.

At the present time, the very high temperature, short-life, applications are largely met by the use of graphite and plastics, while the best heat-resistant alloys, those of nickel and cobalt, serve for high-temperature engine components operating up to about 800-850°C. No wholly successful material exists which can be subjected to practical engineering conditions at temperatures in between these limits, although many materials show a high promise. We shall attempt in the following to give some idea of the reasons why progress in this direction is more difficult than might be anticipated.

2. Survey of the high temperature materials possibilities

In developing materials for high temperature application, the most obvious factor to be considered at the outset is that of their melting-point. A number of elements have melting-points which look very hopeful for high-temperature applications: tungsten (3300°C), tantalum (about 3000°C), rhenium (3180°C), niobium (2468°C), molybdenum (2650°C) and osmium (2700°C), and at somewhat lower temperatures, chromium (1850°C), vanadium (1860°C) and platinum (1769°C).

Of these, rhenium and the platinum metals are not obtainable in sufficient quantities to be useful and very few of these metals can be said to exist as commercial alloys at the present time. The tungsten-base alloys have, of course, been in use as lamp filaments for many years, and the molybdenum alloys, Mo 0.5Ti and Mo 0.5Ti 0.07Zr, are now in production and have achieved some limited applications in missiles and space vehicles. The niobium alloy Nb 0.5Zr is at least in the pilot-plane stage, but the rest may be said to be still experimental. Before embarking on any closer consideration of the refractory metals, we might attempt to see some of their properties in relation to those of other metals. Figure 1 is important in this respect as it shows that the metals of higher melting point have consistently higher activation energies for creep[1]. This implies that the elementary creep process (on the atomic scale) requires a higher energy for its activation, and that, for any selected temperature and stress, the number of sites at which such a process can occur by thermal fluctuations diminishes with increasing melting point. There is, therefore, everything to be gained by using metals of high melting point even though activation energy alone is not the only factor of importance as far as the actual creep rate is concerned. The rate is also dependent upon substructural details, and it is possible for these to affect the creep rate significantly, without necessarily changing the activation energy itself. To be more explicit, if some representative creep rate $\dot{\epsilon}$ (say the steady state creep rate) is taken as an index, and examined over some temperature band, such as 0.4-0.6 T_m, then the rate conforms to an expression of the form $\dot{\epsilon} = A \exp(-Q/RT)$ where Q is the activation energy, R the gas constant, T the absolute temperature and A a constant which is structure-sensitive, as distinct from Q which is sensitive to structure only in certain special cases, which can hardly be reviewed in a paper of this kind.

Unfortunately, the higher the melting point, the greater (usually) is the density, as Figure 2 shows, and this factor can be sufficiently serious to rule out a number of base elements which might otherwise appear attractive. The densities in general lie within a band with a minimum of around 6 to 7 gm/cc, the densities then increasing with melting points above a figure of about 2000°C. The notable exceptions are beryllium (density 1.82) and titanium (density 4.54). Turning now to the elastic modulus variation with melting point (also shown in Figure 2), we find that the values again fall fairly well within a band, as shown. The notable exceptions are again beryllium and titanium, and in addition, zirconium, niobium and tantalum. The last four all show much lower moduli than the general trend indicates - niobium being lower by a factor of two. On the other hand, beryllium appears

not only as the element with a remarkably low density, but as the one element which exhibits a modulus in excess of that indicated by the general trend. Two other elements also show up very well: chromium, with a lower density and a higher modulus than either nickel,iron or cobalt, and molybdenum, with very nearly twice the modulus of these same three elements, but with a density only some 10 to 15 per cent greater. In general we find that the metals of high density/atomic weight ratio are those which have found applications as high temperature materials - that is, the metals with the highest number of atoms per unit volume. This relationship is exhibited by Figure 3: in particular, we note that the elements nickel and cobalt, (and beryllium) have high values of this ratio. Niobium, tantalum and titanium, which show up less favourably than the others in Figure 2, are distinguished again by lower values of density/atomic weight ratios.

We need to examine next whether or not the metals of higher melting point are likely to retain a useful strength at proportionately higher temperatures. If we plot the ultimate tensile stress of a number of materials against the quantity T/T_m, where T is the test temperature and T_m the melting point, both in degrees absolute, we obtain a set of curves of the type shown in Figure 4. We see from this that there is some considerable spread in the critical temperature range for the different metals, but that, as a general rule, the strength fall-off for fairly pure materials begins at between 0.4 and 0.5 of the melting temperature absolute. Alloying can have a quite large effect, and the most obvious feature of this set of curves is probably the great improvements achieved in this way with the nickel alloys. The alloy shown here (Udimet 500) has a composition 56 Ni 19Cr 14Co 4Mo 3Ti 3Al. The curve for molybdenum is close to that for chromium and steel, but titanium shows up as significantly worse when compared in this way - as do some of the refractory metals. Rhenium appears to be about the best from the point of view of both its strength and its critical temperature band, but, as has been said, the metal can hardly be regarded as a serious proposition because of its scarcity.

3. Molybdenum

Molybdenum, from the point of view of its modulus, its strength at temperatures of 1000°C and above, its reasonable density, and its availability, emerges clearly as a base element of some promise. Indeed, if the strengths of some of the present alloys of molybdenum are compared with others on a temperature scale, as shown in Figure 5, then their superiority is at once evident.

However, other factors have to be considered which lead to somewhat less favourable conclusions. In the first place, molybdenum oxide volatilises rapidly above about 700°C and as a consequence heating in air at high temperatures results in a continuous and catastrophic formation and loss of oxide[2]. This effect is illustrated by Figure 6. A great deal of research has been undertaken in connection with the surface protection of molybdenum, covering, for example: alloying; the possibilities of self-regenerative coatings (molybdates); ceramic coatings; cladding; metal-sprayed, diffusion and electroplated coatings. It has been possible to reduce the oxidation rate by a factor of 100 or so by titanium and chromium additions, but the rate is still far too high.

There is a growing feeling that the successful protection of many of the high-temperature alloys must depend upon the evolution of some kind of self-healing coating: zinc coatings on niobium have the required property. As far as molybdenum is concerned, additions of silicon with either cobalt or nickel are beneficial because of the molybdate surface layer which forms at high temperatures. This layer has the required property of self-regeneration after surface damage. Unfortunately, the protection afforded is not maintained over very extended times, as Figure 7 shows[3].

Nickel-base alloys have been used as cladding, with some success, but an additional complication arises with such materials due to the brittle intermetallic compounds formed at the interface. Deformation, or thermal stresses, may result in the opening up of microcracks at this interface, with adverse results.

The general opinion appears to be that sprayed-metal, or electro-deposited metal coatings are the most promising at the moment. Nickel plating is certainly effective[3], as Figure 8 shows, but for gas turbine blades and components subjected to similar conditions of thermal shock and dynamic stress, more resilient coatings are necessary.

Apart from the oxidation limitation, molybdenum has a relatively low recrystallization temperature; this is a serious disadvantage, as the strength developed in the working operations is dissipated at once by the recrystallization process. Additions of other elements to molybdenum, with the object of raising the recrystallization temperature of the solid solution, have been intensively investigated. Figure 9 shows some of the results[3]. Small additions of zirconium or hafnium, or larger additions of titanium, 2 to 3%, are very effective in raising this temperature by some 400°C. Nickel, chromium and cobalt, on the other hand, have the opposite effect. Molybdenum shows a rapid

diffusion through most of the suitable coating metals - nickel, chromium and cobalt. Some idea of the rate of the process may be gained from the fact that alloys of the two metals form by diffusion to a depth of a few thousandths of an inch after 100 hours of heating at about 1000°C, while intergranular diffusion is even faster. To prevent diffusional processes reducing the effectiveness of surface coatings, intermediate layers of other metals - such as gold- have been applied with some success.

Particles of oxide and nitride in the grain boundaries of molybdenum contribute considerably to the low temperature brittleness of the metal. The ductile-brittle transition temperature, as deduced from impact tests, is above 200°C for all the molybdenum tested to date. The tensile transition temperature can, however, be much lower: for very high purity molybdenum a figure as low as -150°C is reported.

The creep resistance of the molybdenum alloys at temperatures of around 1000°C is of outstanding importance. The best of these alloys exhibit creep strengths some three to four times higher than those of the best nickel alloys under equivalent conditions - say at 900°C. The Mo-Ti alloys have been the most widely examined, and for these the carbon content and the carbon/titanium ratio are both factors of importance as far as creep resistance is concerned. The recrystallized alloys, as would be expected, show poorer creep resistance: in fact recrystallization reduces the equivalent creep stresses (say for 100 hr. life at 900°C) by one-half. The principal advantage of the Mo 0.5Ti as compared with, say, the Mo 0.3Nb alloy is that the recrystallization temperature is some 150°C higher (1220°C). Because of this, not only can components be run at a higher temperature, but better coatings (which must be applied at higher temperatures) can be used.

4. Niobium

Both molybdenum and rhenium oxidise catastrophically at elevated temperatures (rhenium above 600°C) in contrast to both tantalum and niobium[4]. In the case of niobium the oxide formed is one of the three possible modifications of Nb_2O_5, niobium pentoxide. The melting point of this pentoxide is 1440°C, and the loss by vaporisation below about 1370°C is not very great: the effect is compared with that of the other refractory metals in Fig. 10. Oxygen embrittlement at lower temperatures is, however, very serious, and some protection is essential. Self-healing zinc coatings are certainly beneficial at temperatures up to about 1100°C, but whether these will be suitable

for higher temperature applications remains to be seen. Both tantalum and niobium have very low ductile-brittle transition temperatures: certainly lower than -195°C.

Niobium in the pure state is readily worked at room temperature and is much more ductile than some of the other refractory metals, such as molybdenum. As noted previously, the modulus of niobium is unfortunately low, and this makes it far less attractive than molybdenum as a structural material. Too little work has been done on niobium, and its possible alloys, to make it possible at the present stage to assess just how important it will prove to be. The experimental niobium alloys have so far been cast in the form of fairly small ingots - six inches in diameter - and the development of large scale frabrication, coating and joining processes is expected to take some years.

5. Cermets

The possibilities of composite materials, such as carbides bonded with metals, have been under intensive study for some time. Many of these are quite successful in their improved heat resistance qualities, titanium carbide in nickel or cobalt alloys for example, but the limited ductility attained has not, so far, enabled them to be applied with any confidence under tensile conditions, or where conditions of thermal or mechanical shock are likely to be encountered. The melting temperatures of the carbides, nitrides and borides of the high temperature elements look very promising; tantalum carbide (3880°C) and tantalum boride (3800°C) for example.

The actual manufacture of such materials naturally raises special difficulties. These we shall not consider here. Basically, the two most suitable methods of production are either sintering a pre-mixed compact of metal and carbide powder, or infiltrating into a sintered carbide skeleton with liquid alloy. The properties of these dispersion-hardened materials are a function of a number of factors, and by no means enough fundamental work has, as yet, been devoted to their proper elucidation. The shapes of the carbide grains, for example, are important because of the stress-concentration effects they introduce; the particles of carbide can undergo considerable grain growth, particularly if the liquid metal temperature is maintained at a high level for some time. For example, titanium carbide particles in cobalt can grow from 1 or 2 microns to about 8 microns in some 30 minutes at the infiltration temperature. As this growth process is diffusion controlled and occurs along the carbide-liquid interface, it should be inhibited by the promotion of wetting (i.e. boundary penetration) by the infiltering alloy. Certain

additions have been tested with the object of affecting the surface energy conditions so that growth does not occur, and a fine particle dispersion is maintained. There is also some evidence that a beneficial heat treatment can be applied to such materials, with a gain in strength and hardness, similar to that applied to the alloys concerned[5]. The actual gain in strength achieved at 1000°C is compared with that of a conventional cobalt alloy in Figure 11. The brittleness is still far too severe: impact values (unnotched) of 4 to 5 foot pounds are common.

The considerable attention devoted to the development of metal-ceramic aggregates has not brought the properties of these materials up to the level required. Some improvements will certainly be made, but it seems unlikely that a really radical advance will come about without some very serious revision of basic principles. The concept of the graded cermet, in which the content of metal binder changes in order to meet localised conditions is a significant one - high metal content in the edges and surfaces of turbine blades, where thermal shock resistance is critical, is a case in point. Infiltration techniques are highly suited to the production of components of this type. Often the properties of such materials can be further improved by cladding with a more ductile high-temperature alloy, and, by this means, not only is the loss of ductility due to oxidation effects much reduced, but the toughness and the resistance to impact generally are also much improved.

At the present time, the experiments on the nature of the fracture of these materials, and the dependence of the fracture characteristics on the material parameters (compositions, particle sizes) are too limited to make generalisations possible. We can, however, say that the characteristics of the interface between the dispersed phase and the metal are of controlling importance. When the wetting is not complete, such as in TiC-Ni systems, the easy fracture path is along the unwetted boundaries between the carbide particles of the relatively large clusters which form. On the other hand, with WC-Co or TiC-NiMo systems, a high degree of wetting is achieved, and fracture occurs through the binder material itself rather than along these boundaries. Islands of metal in the matrix exert interesting effects on the mechanical behaviour, particularly in their apparent ability to absorb transmitted energy by plastic deformation: the deliberate exploitation of this effect may have useful practical consequences.

6. Nickel, Cobalt and Chromium

The striking advance in the properties of the nickel alloys over the last ten years or so leads us to speculate on whether the fundamental reasons for these improvements cannot be applied with benefit to other alloy systems, particularly those with a potentially greater thermal resistance. The present nickel alloys are very complex metallurgically, containing a variety of phases, complex carbides, precipitates and inclusions. Some of these constituents have not been easy to identify, but the feeling now is that the presence of a fine precipitate of Ni_3Al is responsible in large measure for the excellent creep resistance achieved. Such a precipitate is not associated only with the more recent alloys, but is present in the older ones also, Nimonic 80 and Inconel X for example. Views on the direction that high-temperature alloy development should take are somewhat divided. One school of thought takes the view that the locking of dislocations by solute atoms (that is, essentially, the relief of the dislocation stress fields by the diffusion of solute atoms to dislocations) is the most profitable elementary mechanism for increasing the creep resistance. If this is true, then a nice selection of diffusion rates is involved: diffusion should be rapid enough to make dislocation seizure reasonably likely at the temperatures involved, but not so rapid that the dislocations may move quite readily carrying their solute atmospheres with them. As diffusion rates are very sensitive to temperature, then we might well expect to find different atoms more effective in this matter of locking at different test temperatures. Expressed in very general terms, we might say, then, that much might be gained by deliberately adding a variety of solute elements because, for any particular strain rate and temperature, one of these elements might be expected to have a diffusion rate close to the optimum. In practice, matters are by no means as simple as this, as atoms tend to segregate to other structural features (such as boundaries) and to stay there, and in any case not all atoms, from the point of view of size alone, will migrate preferentially to dislocations in the way required.

The opposite view has also been expressed, namely, that the large number of alloying elements which characterise most of the high temperature alloys at the present time are unnecessary, and that a better use of a more restricted range of elements will prove more profitable. There is no evidence as yet to support this proposition. The testing out of new ranges of alloy proportions is a long and laborious business, and we might well expect further improvements in the Ni-Cr-Co-Fe series. Additions of Al-Ti-W and Al-Ti-Mo appear to be hopeful in this connection.

The advantages which the nickel alloys offer are fairly well known, and in the present context we shall merely draw attention to a feature of their behaviour (and of the behaviour of other alloys) likely to be of increasing importance as the lifetime of these alloys is further extended. The high-strength nickel alloys show a minimum in ductility with temperature around 700°C, as do some of the cobalt alloys, the embrittlement being due to the growth of intergranular voids at boundaries normal to the stress axis. These voids grow by the accumulation of vacancies (generated by the plastic deformation) diffusing preferentially to the boundaries subjected to tensile stresses. This type of behaviour is well established in other materials, at suitably elevated temperatures, and the singular sensitivity of these particular alloys is probably associated with the presence, in the boundaries, of void-forming nuclei - precipitates for example. There is no question of such voids forming under compressive stresses. Small additions of boron (0.005 to 0.2 per cent) have been very effective in improving the ductility of some of the high-temperature iron alloys, particularly Fe 26Ni 13Cr 3Mo 1.8Ti. The exact effect boron has is still somewhat uncertain, as its atomic size seems to make it an unlikely interstitial or substitutional element. It is about three-quarters the size of the typical substitutional elements, Fe, Cr, Co, Ni, Mn and V, and larger than the usual interstitials, H, N and C, and thus it might be supposed that if boron were taken into solution the lattice strains would be greater in either case (greater misfit) and consequently the strengthening effect might be proportionately greater as well. In fact, electron photomicrographs show that the additions of boron have a very great effect on the grain-boundary precipitate. This is normally a continuous brittle precipitate, but with boron additions it breaks up into a more discontinuous form and there is also much more evidence of precipitation within the grains. The result is a more ductile alloy, due, it is thought, to the fact that the boron atoms which separate out preferentially along the boundaries prevent the excessive precipitation in this region.

The developments in the cobalt alloys are aimed in the first place at producing higher temperature bearings, nozzles, blades and springs for engine applications. The alloys of this type depend for their strength on dispersions of complex carbides of the M_7C_3, $M_{23}C_6$ and M_6C types. Additional carbide formation can occur at service temperatures and this, on the whole, appears to be beneficial. Some of the cobalt experimental casting alloys - particularly those containing boron - are exceptionally strong (30,000 p.s.i. at 900°C for 100 hr. life). Wrought cobalt alloys have not quite achieved the

creep properties of the best nickel alloys, but their fatigue properties over the temperature range up to 900°C or so give them a superiority over nickel and their moduli of elasticity are also exceptionally good: a linear variation of from 35 x 10^6 to 25 x 10^6 p.s.i. can be achieved over the temperature range 100 to 900°C. Fabrication processes involving some 10 to 20 per cent cold work are reasonable, and these can be followed by a final ageing treatment. The cobalt alloys have really developed from the cobalt-chromium system, and chromium is, in fact, one of the most effective strengthening additions to cobalt. In the unalloyed state, cobalt has very little high temperature resistance - for example the stress for a 100 hr. rupture life of cobalt at 600°C is about 10,000 p.s.i., whereas for the wrought cobalt alloys it is as high as 70,000 p.s.i. Most of the high temperature alloys (those containing Fe, Ni and Co) have additions of at least about 15 per cent chromium with beneficial corrosion-resistance effects. The presence of vanadium or alkaline metals in the fuel ash accelerates the oxidation rate of most high temperature alloys severely, and particularly the attack by vanadium pentoxide. Contents of chromium above 16%, with iron below 30% and vanadium below 2% are helpful in this respect and enable the corrosion to be kept to a satisfactory level.

It may be of interest to record that the alloy 50Co 20Cr 14W 10Ni with Fe, Mn and Si additions (L 605) has been used in the production of honeycomb structures for missiles and aircraft.

A very large number of dispersion-strengthened cobalt materials have been tested. The best of these contain what appeared to be the most finely dispersed particles - as small as 0.02μ . The effect on pure cobalt is very great, but dispersions in Co-Cr alloys have a far less striking effect.

The apparent virtues of chromium as a high temperature material (melting point, modulus, density) have already been commented on. It has, in addition, the advantages of being abundant and of having a good corrosion resistance.

Ductility has, however, always been a problem with chromium. The contents of carbon, nitrogen and oxygen are important in this respect, and must be kept very low. The oxygen content of chromium prepared by the usual processes is high, and as well as this, the metal is highly reactive with the atmosphere in the molten state, so that networks of nitride or carbide can easily be obtained in the cast state. Vacuum melting (which raises new difficulties because of the high vapour pressure of chromium) or inert atmosphere melting has

therefore to be undertaken. The brittleness limitation, at room temperature, is still not solved. The benefits which might be derived from hot-working (elimination of microcracks and the like) are not possible with the high-strength creep-resistant alloys, and this is an obvious limitation.

The view that very high purity chromium would exhibit a much more useful ductility has not been substantiated by experiment. It is true that the tensile ductility is better, and the transition temperature lower, but the values are still not acceptable for engineering purposes. In any case, once the chromium is alloyed (as it must be for high temperature applications) the effects of the high purity condition are negligible.

If the brittleness of chromium is not due to impurities, then we might well consider what the other possibilities are. Chromium is distinguished from the other transition metals in a number of ways. In the first place, the room temperature ductility of many of the other body-centred and hexagonal elements of this group (V, Mo, Ti, Zr, W) is much improved by purification. In addition, chromium shows a number of anomalies in its physical behaviour: for example, the Young's modulus variation with temperature shows two abrupt discontinuities - one at about -160°C and the other at about 35°C. There are similar discontinuities in the temperature variation of electrical resistivity and thermal expansion (as well as of certain other quantities) and these discontinuities are not always coincident. One interesting point that has emerged from recent research is that the lattice contribution to the thermal conductivity of chromium is much higher than with most other metals (about one third of the total) and in this it is similar to beryllium, another element of very limited ductility.

The alloying possibilities of chromium alloys have been examined only to a limited extent, notably the binary systems with Ti, Nb, Ta, Co, Fe, W and Mo. Better high temperature properties can certainly be achieved, but with an increase in the transition temperature. This increase is not usually serious, but it may become a much more serious factor with the more complex chromium alloys. The Cr-Fe-Mo and Cr-Ni-Fe series have received special attention to date, and higher strengths have been obtained, but there is no indication as yet of any better room temperature properties.

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7. Graphite

Graphite is a quite exceptional material in many ways[6]. From the high temperature point of view it has the obvious advantage of a very high sublimation temperature of around 4000°C (there is no liquid phase at atmospheric pressure) coupled with a low density (2.3). The activation energy for sublimation is also very high (170 k cal/mole), which means that the vaporisation process carries away a considerable amount of heat. Graphite is less reactive with oxygen than most metals, but as the oxide is volatile, no protective coating is formed. As the applications for which graphite is really essential at the present time involve very high operating temperatures, 2000°K and above, the oxidation question (or more generally, the chemical reactivity) is the one of greatest concern. It is difficult to separate such effects from those of erosion, as for practical purposes the high temperature conditions are usually associated with high velocity gas streams. Carbide coatings, such as NbC, TaC, and ZrC serve very well up to about 1500°C, above which temperature the carbides themselves oxidise. SiC and B_4C give better protection above this temperature, as well as the nitrides, SiN and BN. Using suitable coating combinations, it has been possible to achieve operating temperatures of about 2000°C; above this no treatment applied up to the present makes any very significant difference to the behaviour.

The actual character of the oxygen attack of graphite is far from simple, and this derives largely from the complex structure of the practical graphites. Whiel the major part of such graphites may be said to be truly graphitic, that is, the structure is well represented by parallel layers of carbon rings, stacked in the graphitic sequence, the boundaries of these graphitic regions necessarily have a more disordered structure with a greater concentration of faults and vacancies. The attack occurs preferentially at these boundary regions, so that a real margin of improvement is possible if these can be reduced or even eliminated. Highly oriented graphitic coatings can be applied to a graphite substrate, and their immediate virtue is that their layer plane orientation can be arranged to give optimum thermal resistance, that is, the planes can lie parallel to the surface. Unfortunately, these pyrolytic graphite coatings have such different thermal expansion properties that in practice the coatings crack off under conditions of very rapid surface heating.

The possibilities of taking advantage of ablation techniques with graphite are fairly good. Ammonium iodide impregnation has worked

quite well, but materials with higher boiling points are really required. Additions of carbides to the graphite mixes have also been investigated. Graphite containing B_4C and SiC does show a better resistance at the more moderate temperatures (1500-1600°C) but again above 2000°C there is no evidence as yet that much improvement will be achieved by this means alone.

Graphite, being highly anisotropic, is not an easy material to design with. Very high local stresses can be created by thermal gradients, and the better the graphite, (that is, the smaller the pore volume) the more severe do thermal shock effects become. The coarser-grained materials, which are not so successful mechanically, do in fact show a very good thermal shock resistance.

Some of the mechanical properties of graphite are encouraging. It certainly increases in tensile strength with temperature up to about 2500°C, at which temperature the strength is twice that at 0°C. This effect is not indicative of a true increase in the strength of the graphitic structure, but rather a consequence of the reduction in the severity of stress concentrators by the localised promotion of plastic strain and the resulting beneficial redistribution in internal stress. Other explanations have been proposed. Graphite is stronger in directions parallel to the layer planes than normal to these, but the ductility is also much less. At room temperature, graphite shows no ductility, and in fact only about 0.5%, as a maximum, is exhibited at 2000°C. Above this temperature more acceptable deformations are possible, so that at about 2800°C 15-20% elongation can be observed. These elongations are achieved with a decreasing density, 15% or so at the higher temperatures, so that voids are certainly formed under these conditions.

Graphite blocks can be joined either by the use of a binder material (or furfuryl alcohol) and re-graphitisation treatment, or brazing is possible using a copper-silver eutectic alloy (heated at 950°C). Zirconium or titanium may also be used as the bond material, applied in vacuo at 1850°C. Niobium has been joined to graphite by this kind of process.

8. Summary in the light of aeronautical and space requirements

The foregoing review of the difficulties which arise when materials are pressed into service at higher temperatures will give some idea of the form that progress in new materials developments might be expected to take. The engineering conditions which are encountered in propulsion

units of advanced design are, however, complex and difficult to assess even for theoretically ideal materials. In practice the mechanical properties alone are not the only factors of concern - although they may be of quite dominant importance - and questions of thermal conductivity, damping capacity, thermal expansion, and so on, inevitably arise. The character of failure in materials subjected to conditions where localised creep is possible, with dynamic stresses superimposed, and with the additional complication of thermal cycling, is a subject which has received very little special attention either fundamentally or from an engineering standpoint. The results that are available indicate that processes which have been regarded so far as separate design questions interact significantly at elevated temperatures. The shorter the life of the machine the more severe the acceptable conditions of stress and temperature may be, and the more important, as a consequence, do such considerations become.

In recent years the construction of more powerful long range missiles has transformed the subject of space travel from a fantasy to a serious scientific study. The great attention devoted to what might be called feasibility studies in this connection has had a remarkable influence on the whole climate of materials thought. Projects which a few years ago would have appeared as wild and extravagant are now much more seriously regarded. The effect of this change of attitude has been not merely to advance directly the technology of the more difficult high temperature materials, but to promote a whole series of studies in metallurgy, chemistry and phsyics which have a bearing on the behaviour and the utilisation of the lesser known elements. Studies on these lines have already yielded results of value, notably in such fields as oxidation kinetics and alloying influences, in questions of cooling systems, ablation theory, transpiration methods and surface protection generally. Considerations of this kind have had to be made within a rather different frame of reference from that usually adopted. In the first place, the individual limitations of the different materials have forced designers and materials specialists to give their attention to the possibilities offered by composite structures which utilise the best features of each of the component materials. Such structures raise a series of new questions: bonding, differential thermal expansion, interdiffusion, stress concentrations, and so on, and materials developments in this context must be seen in terms of these differing and often competitive factors. Quite new exercises in materials design have had to be undertaken and it cannot be said at the present time that these are in anything more than a very tentative form. The second major influence of this new field of

speculation has been to accustom engineers to think in terms of more complicated material systems, not simply in the sense of composite structures but rather in the achievement of practical cooling and protection systems. All such studies must in turn effect some alleviation in the operating conditions of the materials involved in current engine technology, and those which will be concerned in any immediate advance. This, then, might well be an excellent moment to return to the 1000°C class of application armed with the knowledge and the results acquired from the much higher temperature work.

In a recent review, F.R. Morral[7], attributes to a group of the most advanced heat-resisting alloys now used in conventional forms, that is, cast or wrought, operating temperatures for load-carrying applications of 800°C to 1000°C. These are typified by blades and nozzle vanes in gas turbines. Where working stresses are low, the temperatures with these materials, as in ramjet engine components, may reach 1100°C. The same review cites, as the goal for the next ten years, operating temperatures up to 1300°C for gas turbine components and up to 1750°C for ramjets. The formidable task involved in moving towards theseattainments is emphasized by the years of effort which have been necessary to achieve in iron-base, nickel-base and cobalt-base 'conventional' alloys the possibility of reliable functioning in the temperature range 800°C to 1100°C. Refinements of manufacturing technique, such as vacuum melting, may advance these limits by 50°C, but progress beyond this point must depend upon the bringing into service of entirely new classes of materials. We have attempted, in the foregoing, to review the most likely developments in this direction. For engine parts carrying moderate loads, it will be evident that chromium alloys offer a prospect of being competitive with molybdenum and niobium alloys up to 1200°C, and for low stresses to 1350°C. This latter figure seems to be close to the limit for load-carrying applications of molybdenum and niobium. Tantalum and tungsten, because of their very high melting points (3000°C and 3380°C), invite consideration in this connection, but the metallurgical problems of producing these metals in forms and quantities suitable for engineering evaluation have still to be overcome.

A number of non-metallics, borides, carbides, nitrides and graphite, retain useful strength at temperatures higher than those tolerable for any currently available metallic alloy. They all lack the minimum ductility, however, essential for use in the moving parts of engines. This brittleness is, of course, manifest also in all the cermets examined to date. There is, however, some experimental

evidence that this extreme brittleness may not be an inescapable attribute of all ceramics, and a thorough examination, by theoretical and experimental approaches, of this aspect might yield prizes of immense value in making some of the highly refractory non-metallics suitable for engineering use at very high temperatures.

Our past experience in metallurgical developments should encourage us to believe that, from the point of view of strength, at least, the present alloys of molybdenum, niobium and chromium can be greatly improved by alloying. However, the temperature ranges which are now of interest for high temperature machines are such that gas reactions at the surface, particularly oxidation, must be inhibited however high the strengths of the alloys might be.

The surface reactivity question emerges as the one of dominating influence at the present time, and certainly the largest immediate gain in materials applications is dependent on the success or otherwise of surface protection methods. Such a protection is unlikely to be achieved, in the way required, by coatings of the conventional type, but rather by evolving materials with graded properties, so that thermal stresses are better distributed, and also by the use of self-regenerating surface compositions. Quite fundamental investigations are necessary, particularly into the chemistry of these processes, if progress in this direction is to be properly guided. Our efforts otherwise will be both limited and uneconomic.

In the words of Pellini and Harris[8]: "unless some definite sense of direction is evolved to guide the investigator and unless the designer has a better concept of the order of magnitude or importance of the materials effort required, we shall continue to stumble along from one crash program to another. It is essential that management as well as the engineering and scientific staff be appraised of the requirements and the limitations. Unfortunately, venerable experience in either the materials or the design field is no substitute for up-to-date knowledge in this area of entirely new environmental problems".

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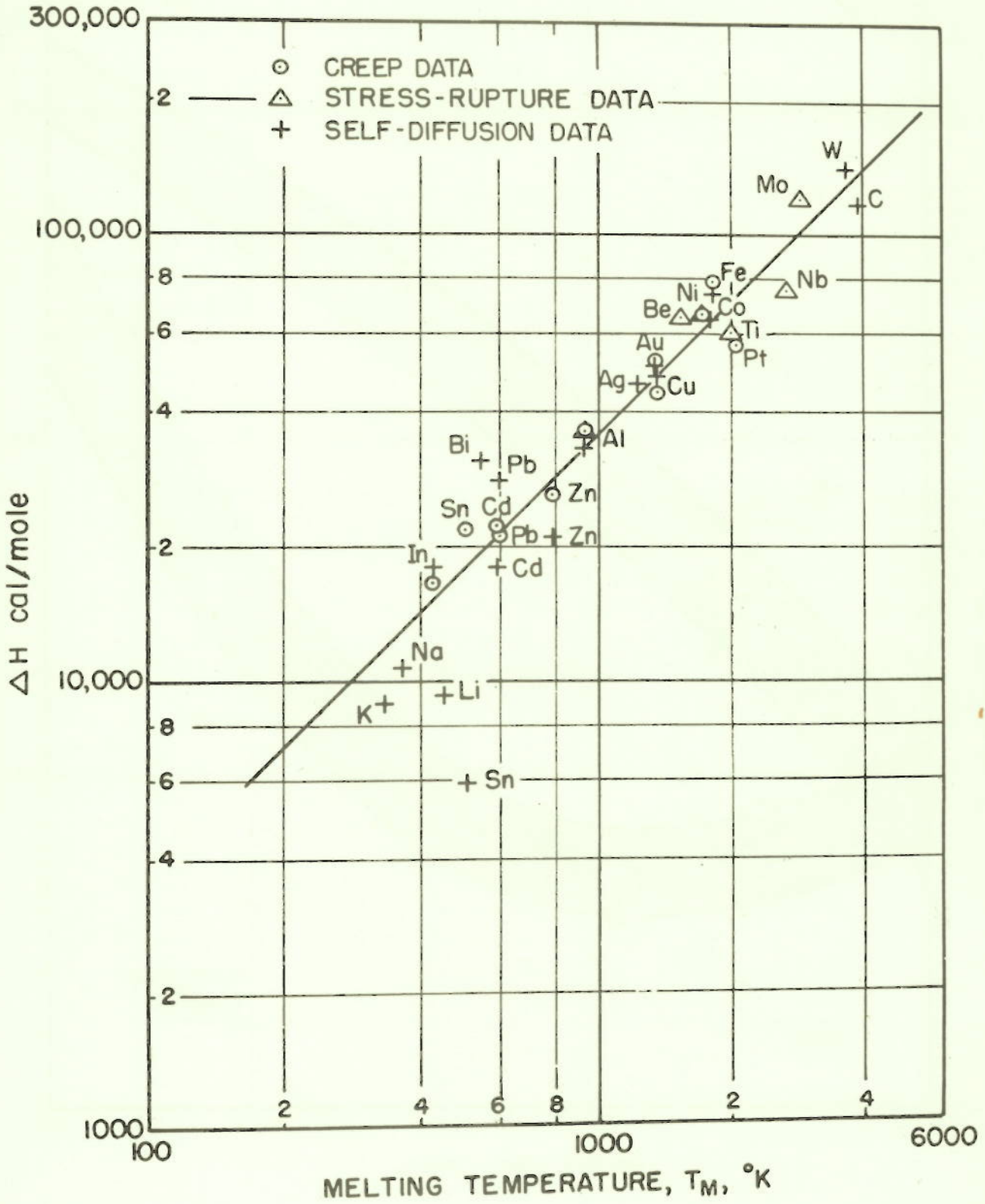

FIG. 1. ACTIVATION ENERGIES FOR CREEP AND SELF DIFFUSION PLOTTED AGAINST MELTING POINTS

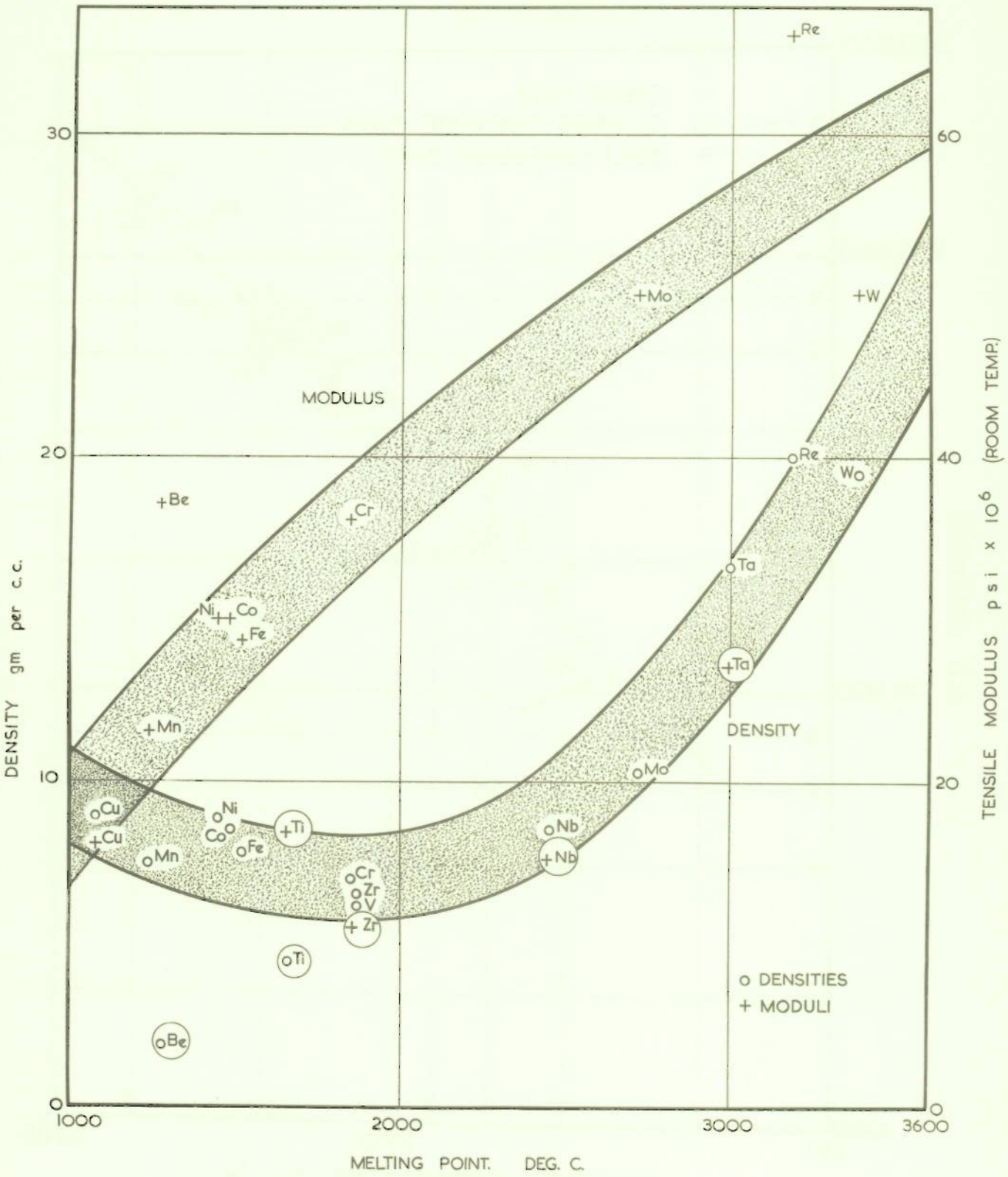

FIG. 2. THE DENSITIES AND THE MODULI OF THE HIGH MELTING POINT ELEMENTS PLOTTED AGAINST MELTING POINT

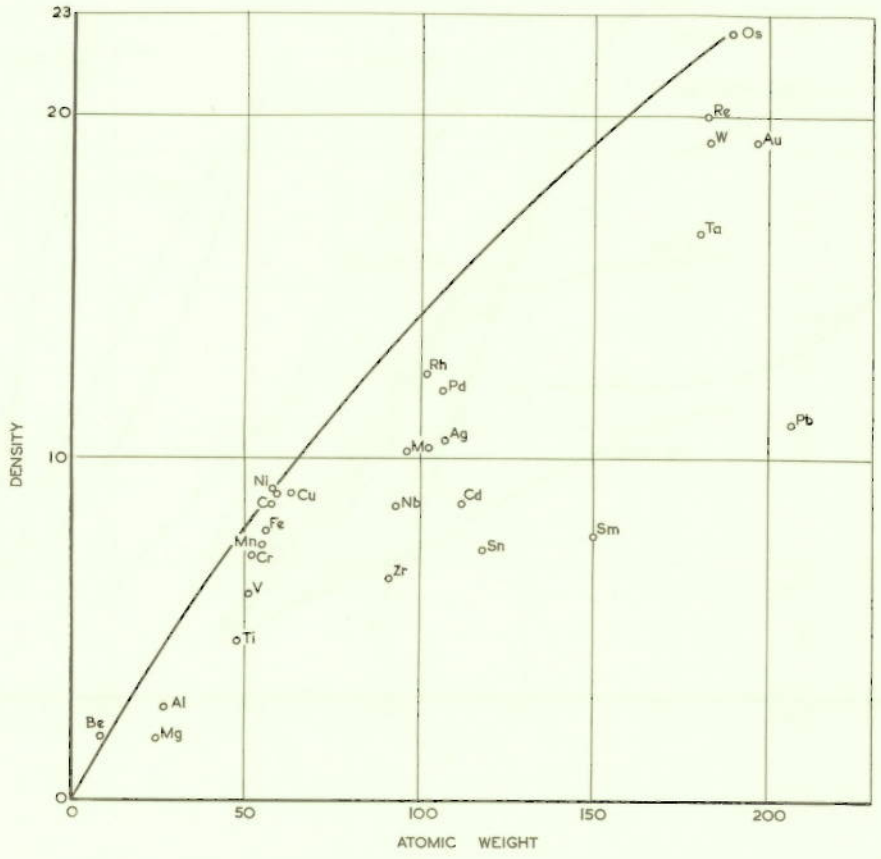

FIGURE 3

FIG. 3. THE DENSITY OF THE MORE COMMON ELEMENTS PLOTTED AGAINST ATOMIC WEIGHT

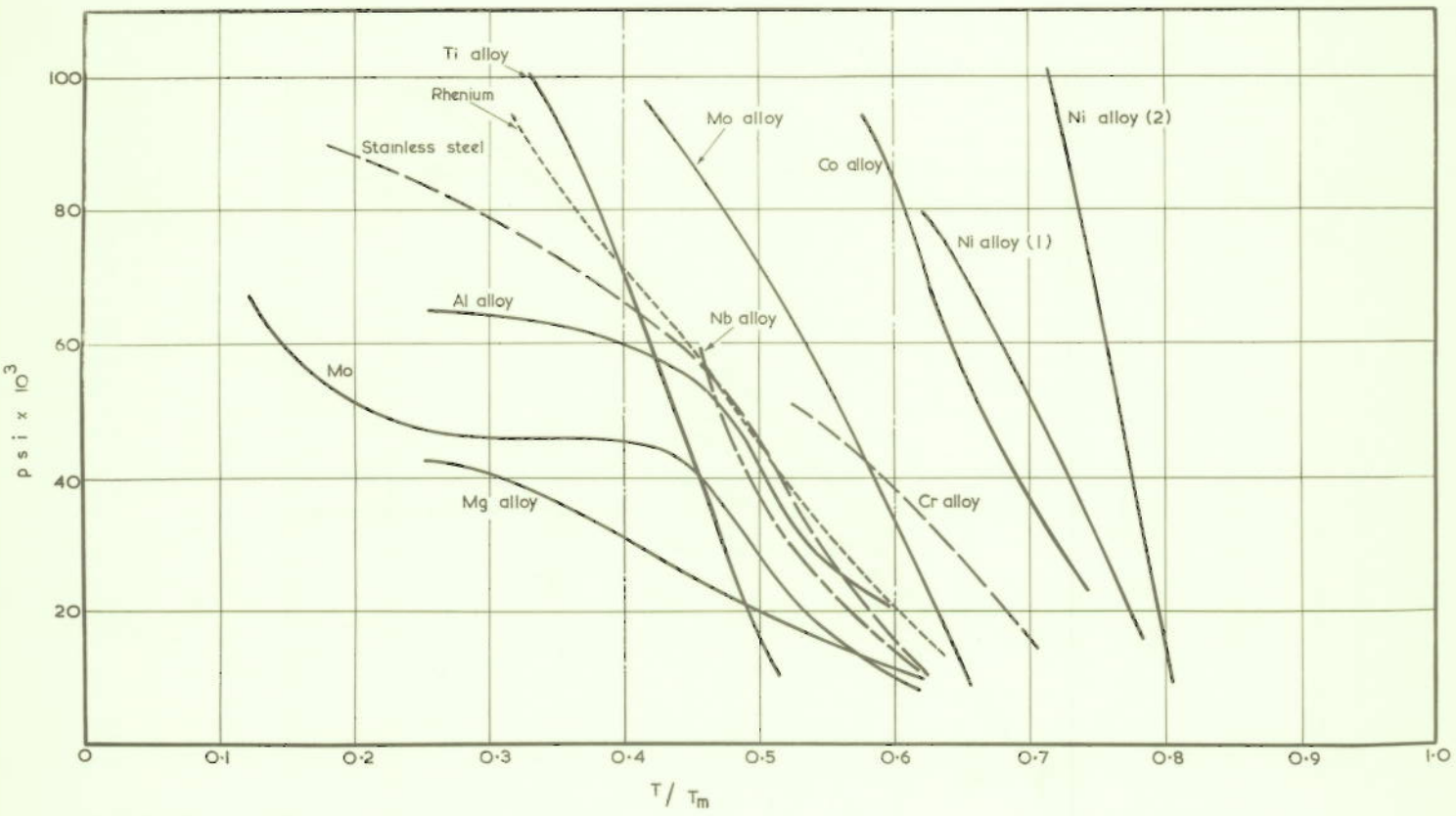

FIG. 4. THE ULTIMATE TENSILE STRENGTH OF VARIOUS ELEMENTS AND ALLOYS PLOTTED AGAINST T/T_m WHERE T IS THE TEMPERATURE AND T_m THE MELTING POINT IN DEGREES K

THE ALLOYS ARE:

Al alloy	Al 2.5Cu 1.5Fe 1.2Ni 0.1Ti (RR 58)
Mg alloy	Mg 0.7Zr 5.5Zn 1.8Th
Nb alloy	Nb 10Ti 10Mo
Ti alloy	Ti 6Al 4V
Mo alloy	Mo 0.5Ti 0.07Zr
Cr alloy	Cr 1Ti
Co alloy	Co 25Cr 5Ni 4W 4Mo (Nb + Ta) 4 B1.0
Ni alloy (1)	Udimet 700:Ni Co19 Cr15
Ni alloy (2)	55 Ni 20Cr 14Co 4Mo 3Ti 3Al

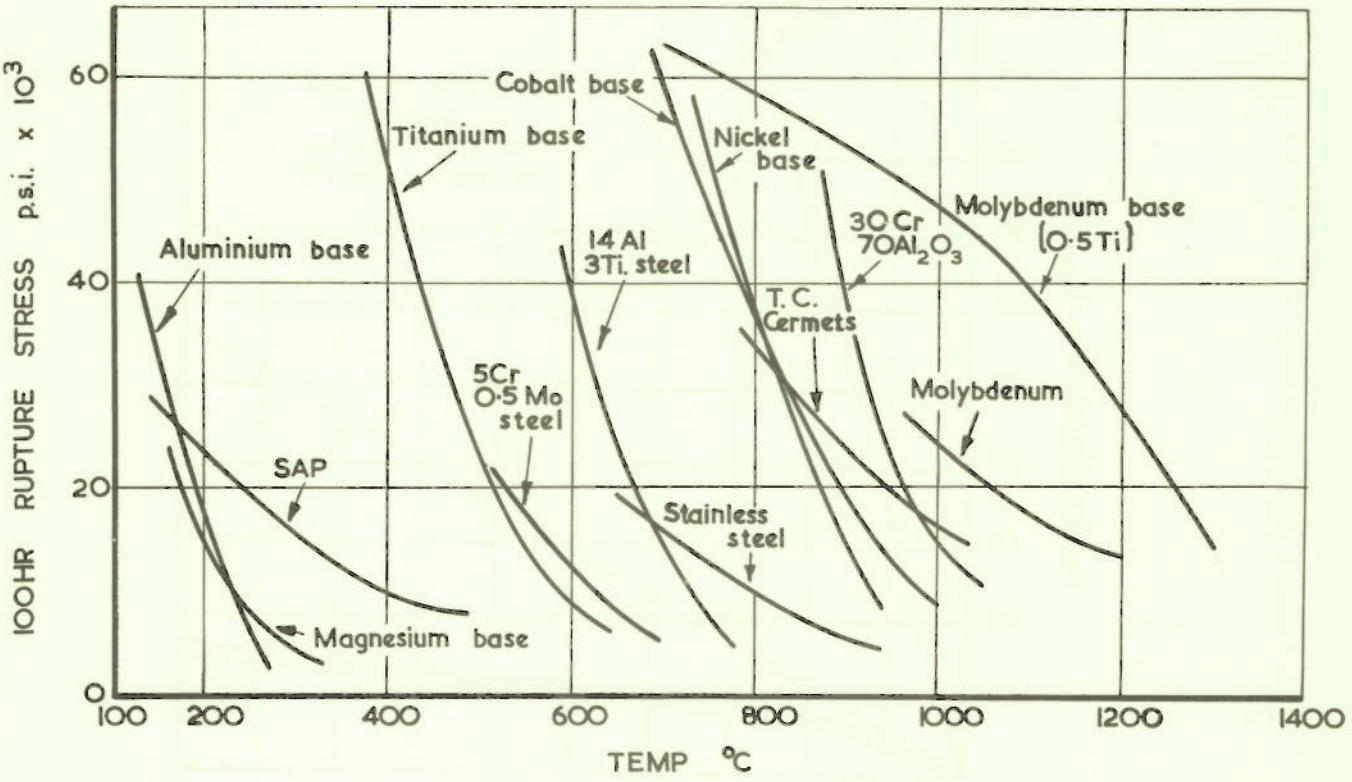

FIG. 5. THE 100hr. RUPTURE STRESS FOR VARIOUS ALLOYS PLOTTED AGAINST TEMPERATURE

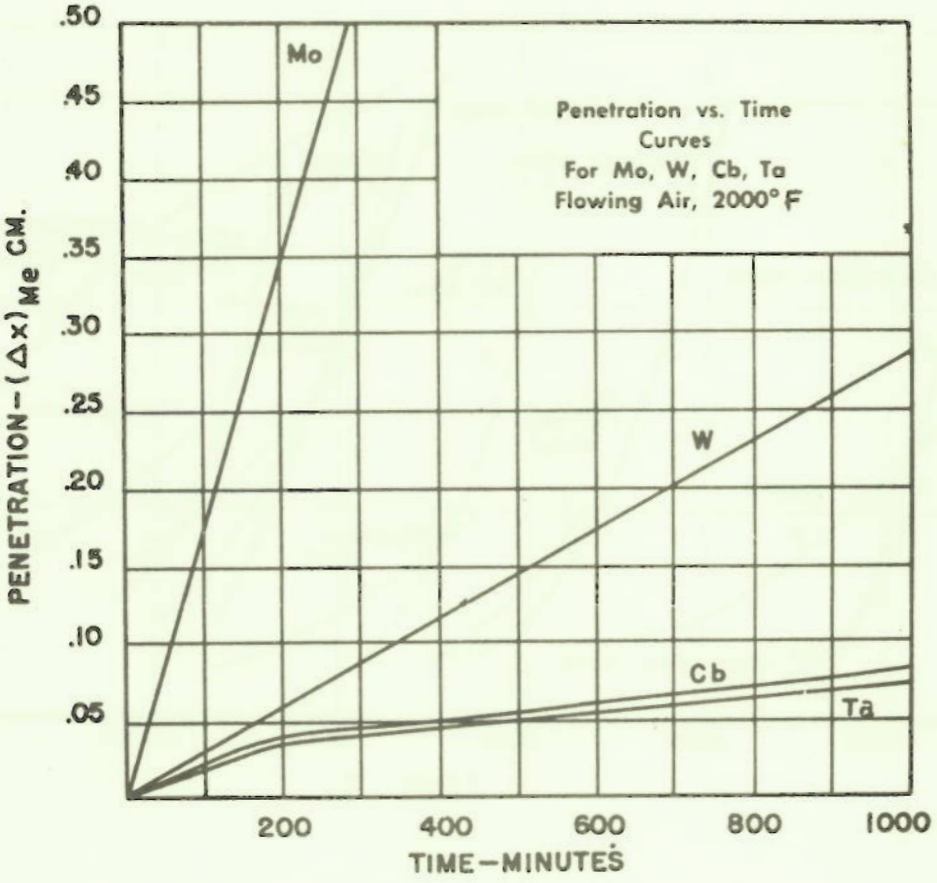

FIG. 6. THE OXIDATION RATE OF MOLYBDENUM COMPARED WITH THAT OF TUNGSTEN, NIOBIUM, AND TANTALUM

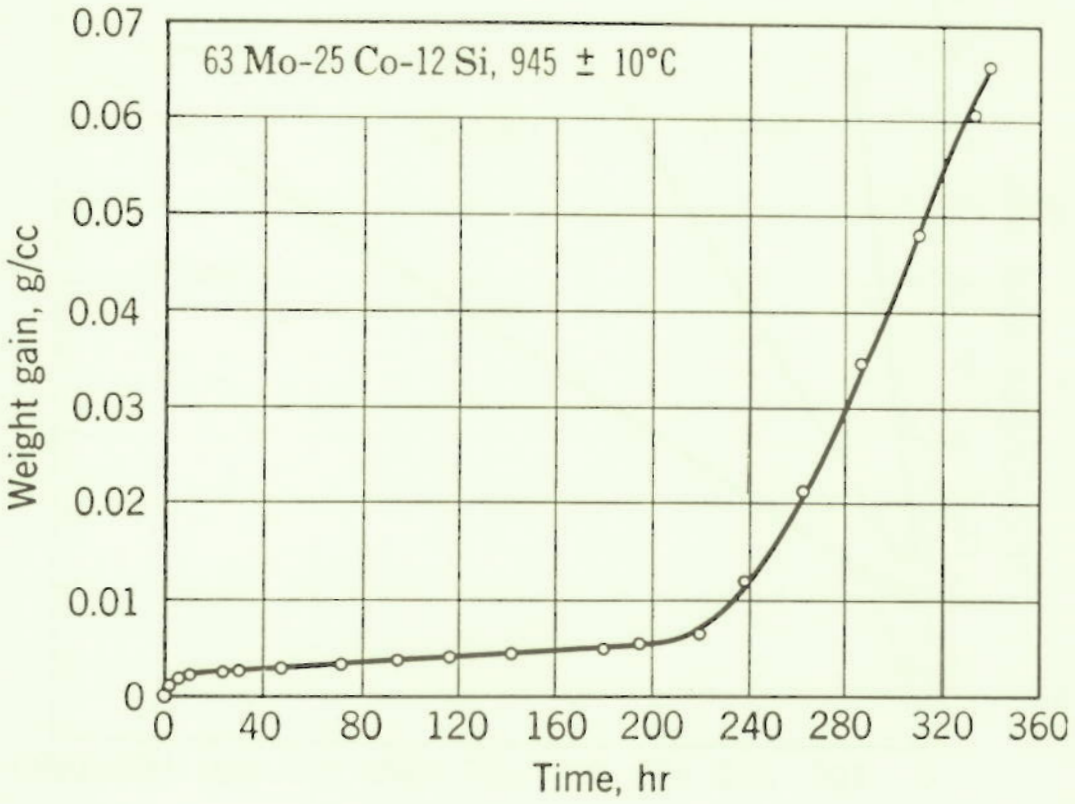

FIG. 7. OXIDATION OF THE ALLOY 63Mo 25Co 12Si AT 945°C

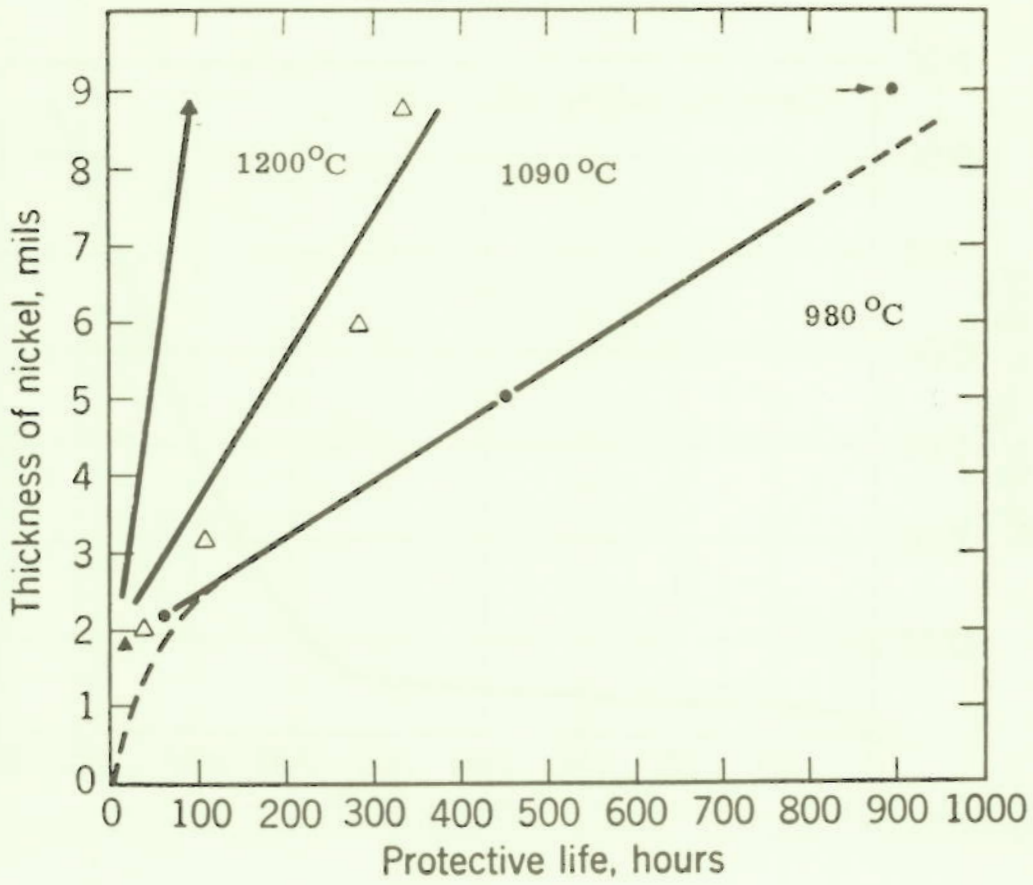

FIG. 8. EFFECT OF VARYING THICKNESSES OF NICKEL ON A BASE OF 0.001 in. Cr IN PROTECTING MOLYBDENUM AT 1200°C, 1090°C AND 980°C

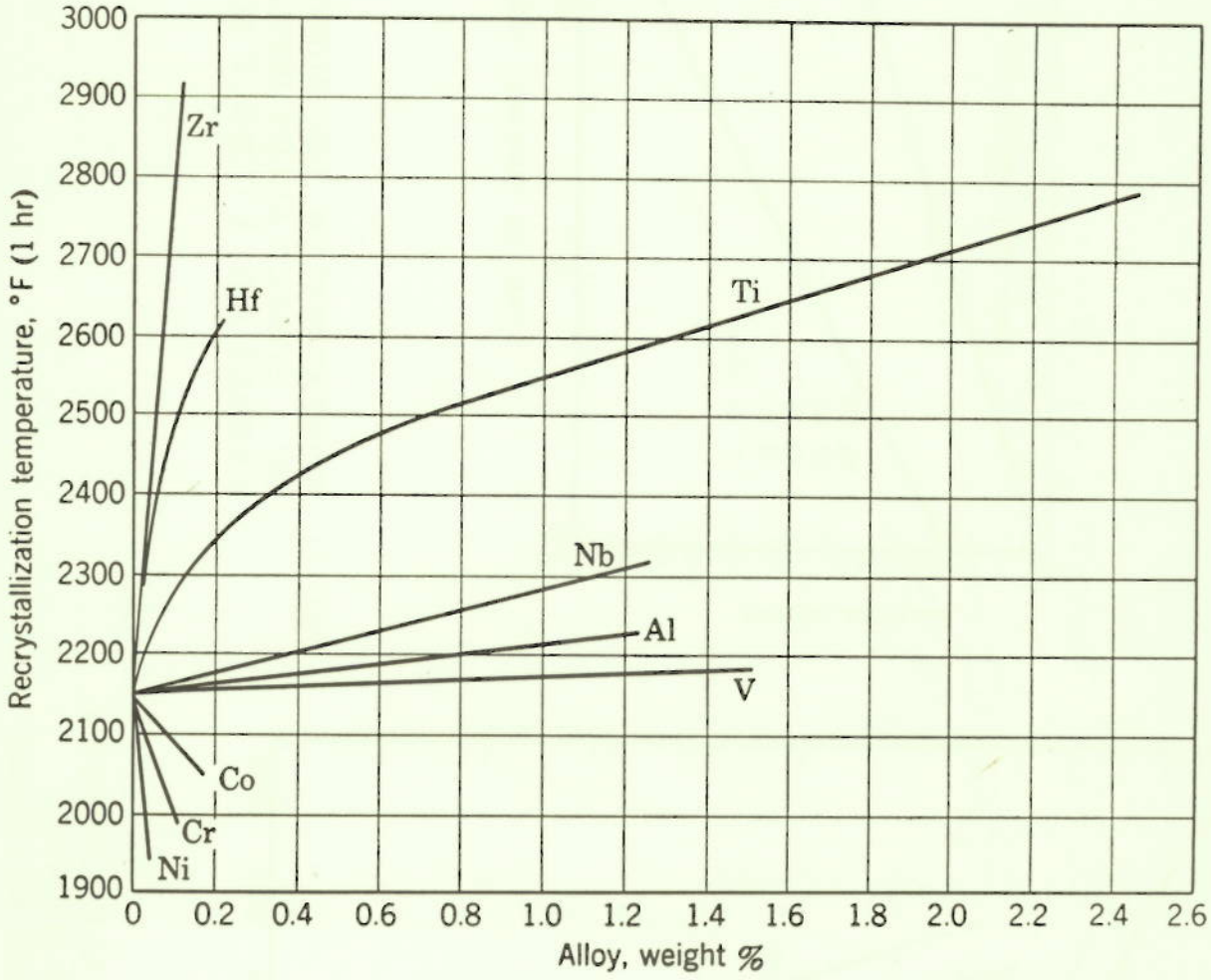

FIG. 9. EFFECT OF ALLOY CONTENT ON THE RECRYSTALLIZATION TEMPERATURE OF WROUGHT MOLYBDENUM

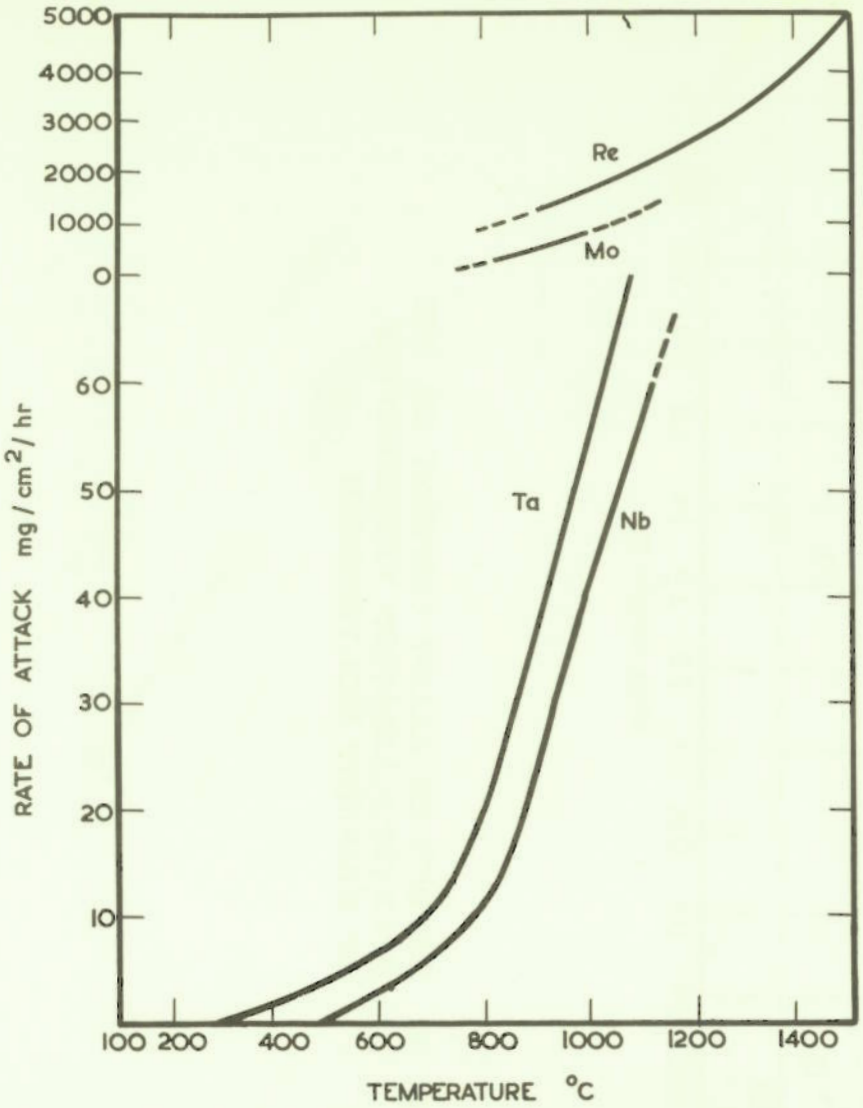

FIG. 10. OXIDATION ATTACK ON TANTALUM, NIOBIUM, RHENIUM, AND MOLYBDENUM SHOWING WEIGHT LOSS AFTER ONE HOUR EXPOSURE AGAINST TEMPERATURE

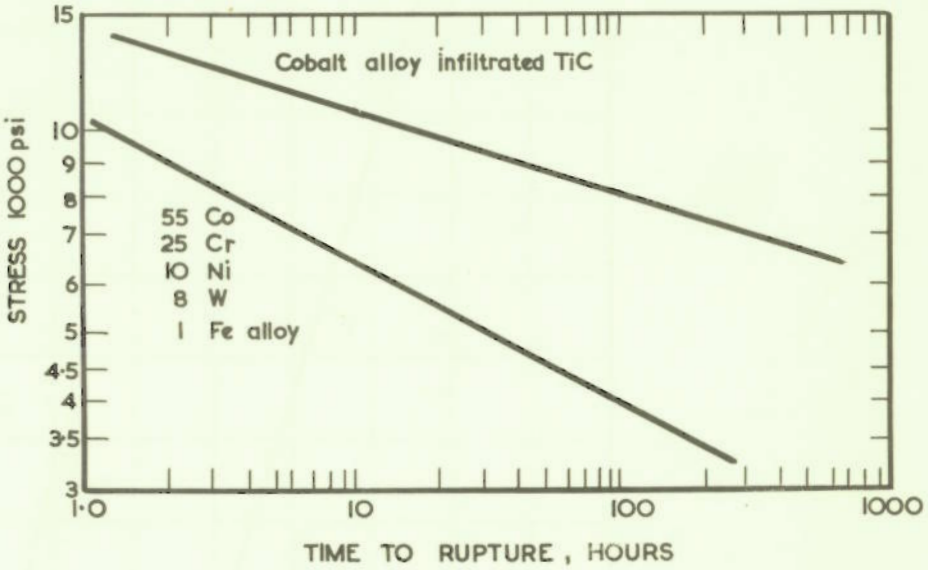

FIG. 11. COMPARISON OF THE RUPTURE STRENGTHS OF A COBALT ALLOY INFILTRATED TiC CERMET AND A COBALT ALLOY AT 1090°C